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Synthesis of cardo-polymers using Tröger's base formation**

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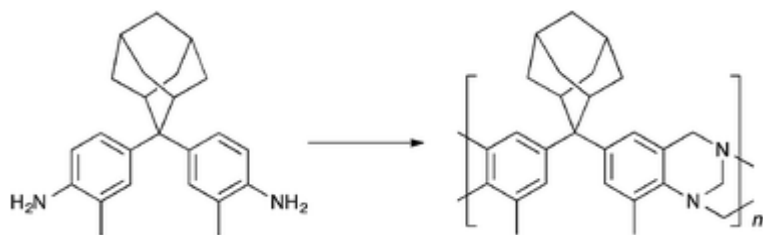
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ARTICLE

Synthesis of cardo-polymers using Tröger's base formation.

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Mariolino Carta,^a Matthew Croad,^b Johannes C. Jansen,^c Paola Bernardo,^c Gabriele Clarizia^c and Neil B. McKeown^{a*}

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A series of novel cardo-polymers was prepared using a polymerisation reaction based on Tröger's base formation. The precursor dianiline monomers are readily available from the reactions between appropriate anilines and cyclic ketones. One adamantyl-based cardo-polymer displays intrinsic microporosity with an apparent BET surface area of 615 m² g⁻¹. This polymer demonstrates a combination of good solubility and high molecular mass facilitating the solvent casting of robust films suitable for gas permeability measurements. The intrinsic microporosity of the polymer provides high gas permeabilities and moderate selectivities with particular promise for gas separations involving hydrogen.

Introduction

There is growing interest in the synthesis of novel membrane materials with improved performances for the separation of mixtures of gases that are required for processes such as CO₂ capture, natural gas upgrading, N₂ or O₂ enrichment of air and H₂ purification.¹⁻⁴ Polymers of Intrinsic Microporosity (PIMs), such as PIM-1 (Fig. 1a), show great promise as adsorbents⁵ and as membrane materials due to their high gas permeability and good selectivity.⁶⁻¹⁹ Recently, we described a novel type of PIM prepared from aromatic diamines by formation of Tröger's Base (TB) units.⁵⁻⁸ TB or more formally 2,8-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine, is a bridged bicyclic amine isolated for the first time in 1887,⁹ although its structure was only assigned correctly in 1935 (Fig. 1b).¹⁰ TB has a V-shaped rigid structure with chiral C₂ symmetry and it has been employed as a building block for various supramolecular assemblies and as a scaffold for molecular replication.^{11,12} The TB unit is also a successful building block for nanoporous polymers.¹³ Recently we have reported that ladder PIMs, prepared via the TB polymerisation of diaminotriptycene or diamino-ethanoanthracene (i.e. PIM-Trip-TB and PIM-EA-TB; Fig. 1c and 1d), provide polymers with exceptional combinations of high gas permeability and selectivity.^{7,8}

Here we describe the synthesis of novel cardo-polymers using TB polymerisation. Cardo-polymers possess cyclic units fused to a single atom within the backbone of the polymer chain.¹⁴ As such they are attractive targets for membrane

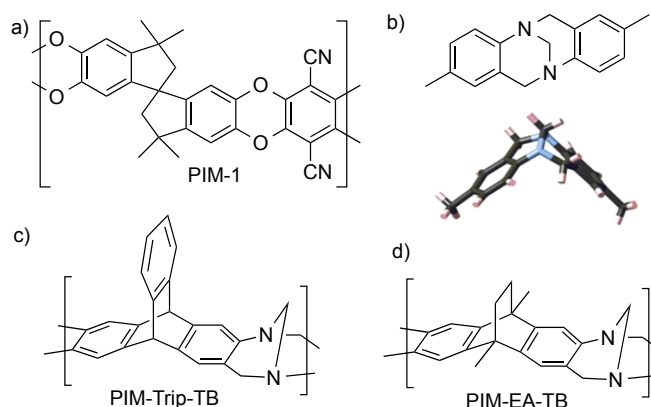


Figure 1. The structures of (a) PIM-1; (b) Tröger's base (c) PIM-Trip-TB and (d) PIM-EA-TB.

polymers as they tend to be relatively rigid and the cardo-unit is attributed with inducing free volume that results in high gas permeability.¹⁵⁻¹⁷ Polymers from monomers consisting of two aniline units linked by cyclohexyl, norbornyl and adamantyl structures in the TB polymerisation are prepared in order to assess the effect of increasing the rigidity of the resulting cardo-polymers. In addition, it was anticipated that blocking one of the ortho positions adjacent to the amino groups, by using monomers derived from *o*-toluidine, might reduce the possibility of cross-linking via further electrophilic substitution during the TB polymerisation.

Experimental

Materials and methods.

Commercially available reagents were used without further purification. Flash chromatography of intermediates was performed on silica gel 60A (35–70 micron) chromatography grade (Fisher Scientific). Melting points were recorded using a Gallenkamp Melting Point Apparatus and are uncorrected. ^1H NMR spectra were recorded in the solvent stated using an Avance Bruker DPX 400 (400 MHz) or DPX 500 (500 MHz) instruments, with ^{13}C NMR spectra recorded at 100 MHz or 125 MHz, respectively. Infra-red spectra were recorded in the range of 4000–600 cm^{-1} using a Perkin-Elmer 1600 series FTIR instrument, either as a thin film or as a nujol mull between sodium chloride plates. All bands are quoted in cm^{-1} . Solid state ^{13}C NMR was obtained using a Varian VNMRs spectrometer operating at 100.56 MHz at Durham University. TGA was performed using the Thermal Analysis SDT Q600 device at a heating rate of 20 $^{\circ}\text{C}/\text{min}$ from room temperature to 1000 $^{\circ}\text{C}$. High-resolution mass spectrometric data were obtained in electron impact ionization (EI) mode on a Waters Q-TOF micromass spectrometer. Low-temperature (77 K) N_2 adsorption/desorption measurements of PIM powders were made using a Coulter SA3100 sorption apparatus. Samples were degassed for 800 min at 120 $^{\circ}\text{C}$ prior to analysis. Gel Permeation Chromatography was carried out using a Viscotek GPC Max1000 system which includes a refractive index detector and two columns (KF-805L Shodex). The analysis used dilute solution of 1 mg of polymer in 1 ml of chloroform at a flow rate of 1 ml min^{-1} . Conformational analysis about the cardo-unit was performed using Spartan 10 software (Wavefunction Inc. Irvine, California, USA).

Monomers 2,2-bis(4-aminophenyl)cyclohexane **1**,¹⁸ 2,2-bis(3-methyl-4-aminophenyl) cyclohexane **2**,¹⁹ 2,2-bis(4-aminophenyl)bicyclo[2.2.1]heptane **3**,²⁰ 2,2-bis(4-aminophenyl)adamantane **5**,²⁰ were prepared following literature procedures.

Synthetic procedures

2,2-Bis(3-methyl-4-aminophenyl)bicyclo[2.2.1]heptane **4** Norcamphor (7.00 g, 63.6 mmol), 2-methylaniline (20.4 ml, 191 mmol) and 2-methylaniline hydrochloride (18.28 g, 127 mmol) were mixed together at room temperature. The mixture was heated to 150 $^{\circ}\text{C}$ and stirred for 20 hours under nitrogen before the reaction was quenched by addition of water (100 ml). After stirring for an hour, aqueous ammonia (35%, 100 ml) was added and after brief stirring the crude product was extracted with chloroform (3 x 100 ml). The solvent was removed under reduced pressure, giving a brown oil, which was then passed through a silica column (6:4 hexane:ethyl acetate). On evaporation of solvent the product was obtained as a cream powder (4.95 g, 25%). Mp 98 – 100 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ ppm 1.16 (1H, m), 1.30 (2H, m), 1.44 (2H, m), 1.70 (1H, m), 2.10 (6H, s), 2.23 (2H, m), 2.33 (1H, s), 3.07 (1H, s), 3.38 (4H, s), 6.54 (2H, d, $J = 8.2$ Hz), 6.97 (4H, m); ^{13}C NMR

(100 MHz, CDCl_3) δ ppm 17.7, 24.8, 29.8, 38.3, 43.5, 44.8, 54.8, 114.8, 121.8, 122.0, 125.1, 126.2, 129.1, 130.0, 139.6, 141.1, 141.4, 143.7; HRMS Calc. for $\text{C}_{21}\text{H}_{26}\text{N}_2$ $m/z = 306.2096$, found 306.2097; IR (NaCl): 3449, 3368, 3219, 2958, 2870, 2734, 2240, 1869, 1738, 1623, 1582, 1505, 1454, 1407, 1379, 1288, 1217, 1156, 1068, 1033 cm^{-1} .

2,2-bis(3-methyl-4-aminophenyl)adamantane **6** 2-Adamantanone (20.00 g, 133 mmol), 2-methylaniline (42.8 ml, 399 mmol) and 2-methylaniline hydrochloride (42.06 g, 293 mmol) were mixed together at room temperature. The mixture was heated to 180 $^{\circ}\text{C}$ and stirred for 20 hours under nitrogen. The reaction was then quenched by addition of water (200 ml), and stirred for an hour before aqueous ammonia (35%, 200 ml) was added. After brief stirring the crude product was extracted with chloroform (3 x 300 ml). The solvent was removed under reduced pressure, giving a brown oil, which was then passed through a silica column (6:4 hexane:ethyl acetate). Finally, washing the material with methanol (100 ml) gave the product as a cream powder (16.08 g, 35%). Mp 261–263 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ ppm 1.71 (6H, br. s), 1.79 (2H, s), 2.10 (10H, m), 3.12 (6H, m), 6.55 (2H, d, $J = 8.0$ Hz), 7.05 (4H, m); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 17.9, 27.8, 32.0, 33.5, 38.3, 49.0, 115.3, 122.3, 124.1, 127.7, 139.7, 141.0; HRMS Calc. for $\text{C}_{24}\text{H}_{30}\text{N}_2$ $m/z = 346.2409$, found 346.2408 gmol^{-1} ; IR (NaCl): 3448, 3376, 3019, 2910, 2853, 2734, 2676, 2239, 1866, 1624, 1508, 1469, 1450, 1411, 1378, 1359, 1308, 1288, 1216, 1149, 1119, 1101, 1076, 1033 cm^{-1} .

General procedure for TB-based polymerisation. The diamine monomer (7.51 mmol) was dissolved in trifluoroacetic acid (20 ml) with stirring at 0 $^{\circ}\text{C}$. Once dissolved, dimethoxymethane (3.32 ml, 37.57 mmol) was added and the mixture left stirring under nitrogen for 40 hours. The reaction was then quenched by addition of water (100 ml) and aqueous ammonia (35%, 100 ml). After stirring for 4 hours the precipitated polymer was collected by filtration then washed with water (100 ml) and acetone (100 ml). Fully soluble polymers were dissolved in chloroform (100 ml) and reprecipitated by addition of hexane (150 ml). Insoluble polymers were ground to a fine powder before being washed in refluxing acetone, THF and methanol (100 ml), each for 16 hours. The polymer was then collected by filtration and dried under vacuum.

Cy-TB. Using the general procedure, 2,2-bis(4-aminophenyl)cyclohexane **1** gave the product as a predominately insoluble cream coloured powder (2.07 g, 91%, based on repeat unit). BET surface area = 50 $\text{m}^2 \text{g}^{-1}$; total pore volume = 0.21 ml g^{-1} at $p/p^{\circ} = 0.98$; GPC (based on polystyrene standard, using a small soluble portion) $M_n = 5,800$, $M_w = 35,300 \text{ gmol}^{-1}$; ^{13}C NMR (100 MHz, *solid state*) δ ppm 23.8, 36.8, 44.0, 47.4, 58.9, 66.9, 127.5, 141.0, 146.9.

TB-Cy-Me. Using the general procedure, 2,2-bis(3-methyl-4-aminophenyl)cyclohexane **2** (2.00 g, 6.80 mmol) gave a cream powder (1.80 g, 87% based on the repeat unit). BET surface area = 30 $\text{m}^2 \text{g}^{-1}$; total pore volume = 0.09 ml g^{-1} at $p/p^{\circ} = 0.98$; TGA (nitrogen): weight loss due to thermal degradation started at 332 $^{\circ}\text{C}$ and totaled 59.4%, GPC (based on polystyrene

standard) $M_n = 44,300$, $M_w = 118,400$ g mol^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 1.43 (6H, br. s), 2.10 (4H, br. s), 2.32 (6H, br. s), 3.90 (2H, br. m), 4.22 (2H, br. s), 4.48 (2H, br. m), 6.63 (2H, br. s), 6.83 (2H, br. s); ^{13}C NMR (100 MHz, *solid state*) δ ppm 17.4, 23.2, 26.8, 37.6, 44.5, 47.2, 55.5, 67.9, 128.0, 144.0, 136.7.

TB-Nor. Using the general procedure, 2,2-bis(4-aminophenyl)bicyclo[2.2.1]heptane **3** (2.00 g, 7.19 mmol) gave a partially insoluble brown powder (1.30 g, 57%, based on repeat unit). BET surface area = $4 \text{ m}^2 \text{ g}^{-1}$; total pore volume = 0.03 ml g^{-1} at $p/p^\circ = 0.98$; GPC (soluble fraction based on polystyrene standard) $M_n = 1,700$, $M_w = 4,500$ g mol^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 1.30 (6H, br. m), 2.16 (3H, br. m), 2.99 (1H, br. s), 4.11 (4H, br. m), 4.57 (2H, br. s), 6.87 (6H, br. m); ^{13}C NMR (100 MHz, *solid state*) δ ppm 26.2, 39.1, 42.2, 45.9, 55.7, 56.7, 67.3, 127.3, 145.9.

TB-Nor-Me. Using the general procedure, 2,2-bis(3-methyl-4-aminophenyl)bicyclo[2.2.1]heptane **4** (3.00 g, 9.80 mmol), gave a cream powder (1.94 g, 58% based on repeat unit). BET surface area = $70 \text{ m}^2 \text{ g}^{-1}$; total pore volume = 0.37 ml g^{-1} at $p/p^\circ = 0.98$; TGA (nitrogen): weight loss due to thermal degradation started at 350°C and totaled 58.5%, GPC (based on polystyrene standard) $M_n = 13,900$, $M_w = 31,600$ g mol^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 1.15 (3H, br. m), 1.44 (3H, br. m), 2.08 (3H, br. m), 2.31 (6H, br. s), 3.03 (1H, br. s), 3.88 (2H, br. s), 4.17 (2H, br. s), 4.47 (2H, br. m), 6.69 (2H, br. m), 6.91 (2H, br. m); ^{13}C NMR (100 MHz, *solid state*) δ ppm 17.2, 25.0, 39.0, 43.6, 55.6, 67.6, 126.8, 143.6, 148.3.

TB-Ad. Using the general procedure, 2,2-bis(4-aminophenyl)adamantane **5** (2.00 g, 6.06 mmol), gave a partially insoluble cream powder (1.94 g, 88% based on repeat unit). BET surface area = $50 \text{ m}^2 \text{ g}^{-1}$; total pore volume = 0.25 ml g^{-1} at $p/p^\circ = 0.98$; GPC (soluble portion based on polystyrene standard) $M_n = 4,200$, $M_w = 14,800$ g mol^{-1} ; ^{13}C NMR (100 MHz, *solid state*) δ ppm 28.5, 33.7, 45.0, 50.4, 60.6, 68.4, 124.8, 127.7, 144.7, 145.7.

TB-Ad-Me. Using the general procedure, 2,2-bis(3-methyl-4-aminophenyl)adamantane **6** (5.00 g, 14.43 mmol) gave a cream powder (3.19 g, 58% based on repeat unit). BET surface area = $615 \text{ m}^2 \text{ g}^{-1}$; total pore volume = 0.41 ml g^{-1} at $p/p^\circ = 0.98$; TGA (nitrogen): weight loss due to thermal degradation started at 470°C , GPC (based on polystyrene standard) $M_n = 31,500$, $M_w = 113,000$ g mol^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 1.67 (8H, br. m), 1.91 (4H, br. s), 2.29 (6H, br. s), 3.03 (2H, br. s), 3.88 (2H, br. m), 4.13 (2H, br. m), 4.46 (2H, br. s), 6.74 (2H, br. s), 7.00 (2H, br. s); ^{13}C NMR (100 MHz, *solid state*) δ ppm 16.7, 28.5, 33.9, 38.5, 50.0, 55.7, 67.9, 121.7, 127.6, 132.3, 143.7.

Film formation

Thin film flat membranes were prepared by solvent evaporation from a 2-4% w/v solution of the novel TB polymers in chloroform (typically 600 mg in 18 ml of chloroform). The solution was filtered through glass wool to remove dust and poured into a 9 cm circular Teflon mould. The film was allowed to form by slow solvent evaporation for 96 h in a

desiccator at room temperature. In order to obtain alcohol treated films the as cast film was immersed overnight in MeOH and was dried for 24 h under ambient conditions.

Gas permeation procedure

Single gas permeation measurements were carried out at 25°C at a feed pressure of 1 bar in a fixed volume/pressure increase apparatus (GKSS, Germany) in the time lag mode.²¹ The rotary vacuum pump was equipped with an alumina trap to avoid oil contamination of the membrane. The instrument is equipped with PC controlled pneumatic valves to allow response times of less than 0.5 s.²² The gases were tested in the following order: He, H_2 , N_2 , O_2 , CH_4 , and CO_2 . Before each experiment the membrane sample was carefully evacuated (10^{-2} mbar) to remove previously dissolved gas species. Circular samples with an effective diameter of 2.14 cm^2 were used. The thickness of the films was determined using a digital micrometer (Mitutoyo, model IP65). The films were first tested as-cast and then after MeOH treatment. The permeability coefficient, P , and diffusion coefficient, D , were determined as described previously.²² The gas permeability is expressed in barrer ($1 \text{ barrer} = 10^{-10} \text{ cm}^3 \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1} = 3.35 \times 10^{-16} \text{ mol m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$). The solubility coefficient, S , for the gas in the polymer matrix was evaluated indirectly, assuming the validity of the solution-diffusion permeation model.²³

$$S = P/D \quad (1)$$

The ideal selectivity for a pair of gases, A and B, was calculated as the ratio of the individual single gas permeabilities. It can be decoupled into solubility-selectivity and diffusivity-selectivity:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{S_A}{S_B} \cdot \frac{D_A}{D_B} \quad (2)$$

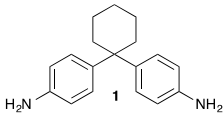
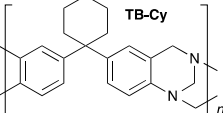
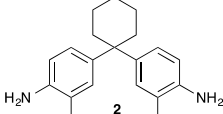
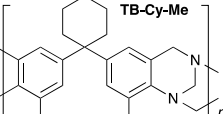
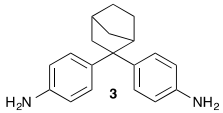
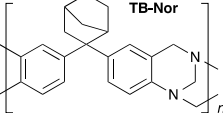
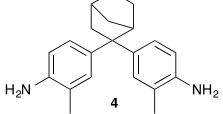
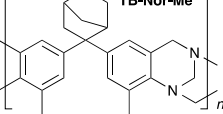
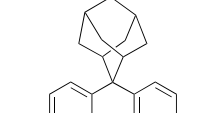
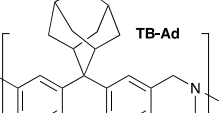
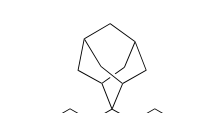
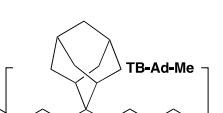
Results and discussion

Polymer synthesis

The required diamine monomer precursors **1-6** to the target cardo-polymers were prepared using the reactions between cyclohexanone, norcamphor or 2-adamantanone and either aniline or 2-methylaniline.¹⁸⁻²⁰ It proved convenient to use a 1:1 mixture of the aniline and its hydrochloride salt, the latter providing the acid required for the reaction.

For each of the six monomers, the TB polymerisation reactions were performed using an excess of dimethoxymethane (5:1 molar ratio to monomer) as the methylene source and trifluoroacetic acid as both solvent and acid catalyst. The reactions were carried out initially at 0°C , after which it was allowed to gradually reach ambient temperature, where the reaction was continued, up to a total reaction time of 72 hours. For monomers **1**, **3** and **5** a mixture of soluble and insoluble product was obtained, the latter

Table 1. Properties of the Troger's base (TB) polymers.

Monomer	Polymer	Yield (%)	Solubility ^a	$M_w \times 10^3$ (g mol ⁻¹)	PDI (M_w/M_n)	BET surface area (m ² g ⁻¹)	Pore Volume ^c (cm ³ g ⁻¹)
 1	 TB-Cy	91	P	35 ^b	6.1 ^b	50	0.21
 2	 TB-Cy-Me	87	S	118	2.7	30	0.09
 3	 TB-Nor	57	P	4.5 ^b	2.6 ^b	4	0.03
 4	 TB-Nor-Me	58	S	31	2.3	70	0.37
 5	 TB-Ad	88	P	15 ^b	3.5 ^b	50	0.25
 6	 TB-Ad-Me	58	S	113	3.6	615	0.41

^aS = soluble in chloroform, P = only partially soluble in chloroform; ^bsoluble fraction; ^ccalculated from nitrogen adsorption at $p/p^o = 0.98$.

attributed to crosslinking. In contrast, monomers **2**, **4** and **6** gave products that were fully soluble in chloroform. Therefore, the presence of a methyl group adjacent to each amino group successfully blocks cross-linking which is likely to be caused by additional electrophilic substitution reactions with the excess dimethoxymethane. The properties of the polymer products are summarised in Table 1. For each polymer, solution ¹H NMR as well as solid state ¹³C NMR are consistent with their expected structures. Thermal gravimetric analysis indicated that the polymers are stable up to at least 300 °C.

Gel permeation chromatography (GPC) confirmed that the polymers **TB-Cy-Me** and **TB-Ad-Me**, derived from monomers **2** and **6**, respectively, are of high average molecular mass ($M_w > 100,000$ g mol⁻¹). Robust self-standing films could be prepared from these polymers using simple solution casting. Unsurprisingly, the soluble portions of **TB-Cy**, **TB-Nor** and **TB-Ad**, from monomers **1**, **3** and **5**, respectively, are of relatively low average molecular mass.

Microporosity and gas permeability

Nitrogen adsorption at 77 K showed that only the polymer **TB-Ad-Me** possesses intrinsic microporosity, as demonstrated by significant adsorption at low values of relative pressure (Fig. 2). An apparent BET surface area of 615 m² g⁻¹ could be calculated from the isotherm, which is less than most other PIMs examined for gas permeability (e.g. PIM-1, PIM-EA-TB and PIM-Trip-TB have reported values of ~780, 1000 and 900 m² g⁻¹, respectively).^{7,8,24} Intrinsic microporosity is obtained from a combination of non-linear shape, rigidity and lack of conformational freedom leading to an inability to pack space efficiently. Each cardo-polymer will have non-linear chains due to the V-shaped TB unit and the roughly tetrahedral configuration around the central carbon of the cardo-unit (Fig. 3a). Therefore, the unique generation of intrinsic microporosity by **TB-Ad-Me** for these cardo-polymers is likely to arise due to the greatly hindered rotation of the phenyl groups attached to

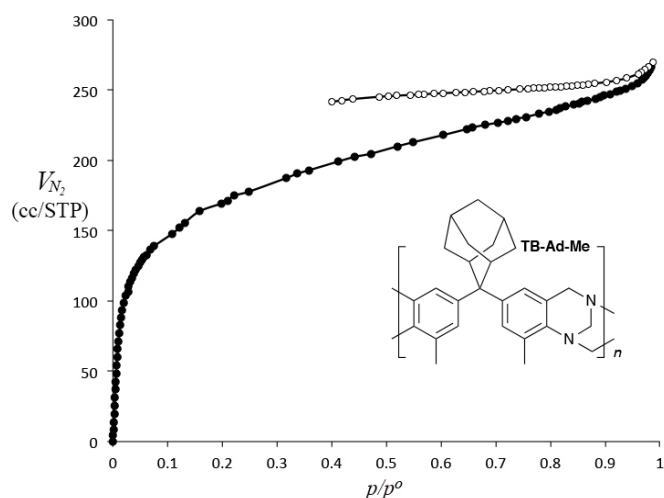


Fig. 2. The nitrogen sorption isotherm of TB-Ad-Me (77 K).

the bulky adamantyl unit. Hence, the energy costs of rotation of the various TB phenyl groups about the C-C single bond within the cardo-unit were calculated and the results are shown in Fig. 3b. The bulky adamantyl unit presents an energy barrier of ~ 65 kJ mol $^{-1}$, with a narrow energy well, whereas that for rotation of the TB phenyl groups attached to the cyclohexyl unit is ~ 28 kJ mol $^{-1}$, with a broad energy well. The unsymmetrical norbornyl unit provides a different energy barrier to rotation for each of the attached TB phenyl groups (~ 42 and ~ 57 kJ mol $^{-1}$) but for each the energy well is much broader than that due to the adamantyl unit indicating greater conformational freedom.

The intrinsic microporosity of TB-Ad-Me prompted the study of the gas permeability of its cast film. The film was tested in three different states: as cast, after methanol treatment and six months after methanol treatment (Table 2). Soaking in methanol is known to remove the residual solvent from PIM films and reverses physical aging (i.e. loss of free volume over time). The order of magnitude gain in gas permeabilities for TB-Ad-Me after methanol treatment is more significant than previously observed for PIM-1 (2-3 times increase) but is similar to that found for PIM-EATB. The effect is likely to be related to greater residual solvent retention due to strong interactions between the TB amine functionality and chloroform (or adsorbed water). Overall the gas permeabilities for methanol treated TB-Ad-Me are lower than for PIM-1, PIM-Trip-TB or PIM-EA-TB, which is consistent with its lower apparent BET surface area. Nevertheless, the combination of moderately high permeabilities and moderately high gas selectivities is promising.

The potential of a new polymer for a particular gas separation is assessed by placing its permeability data on plots of $\log P_x$ versus $\log \alpha_{x/y}$ where P_x is the permeability of the more permeable gas x and $\alpha_{x/y}$ is the ideal selectivity of the polymer for gas x over gas y (i.e. P_x/P_y). For a membrane material both high permeability and selectivity are desirable. In 1991 Robeson established an upper bound on such plots that represents the data for the best performing polymers versus the trade-off between permeability and selectivity for a given gas

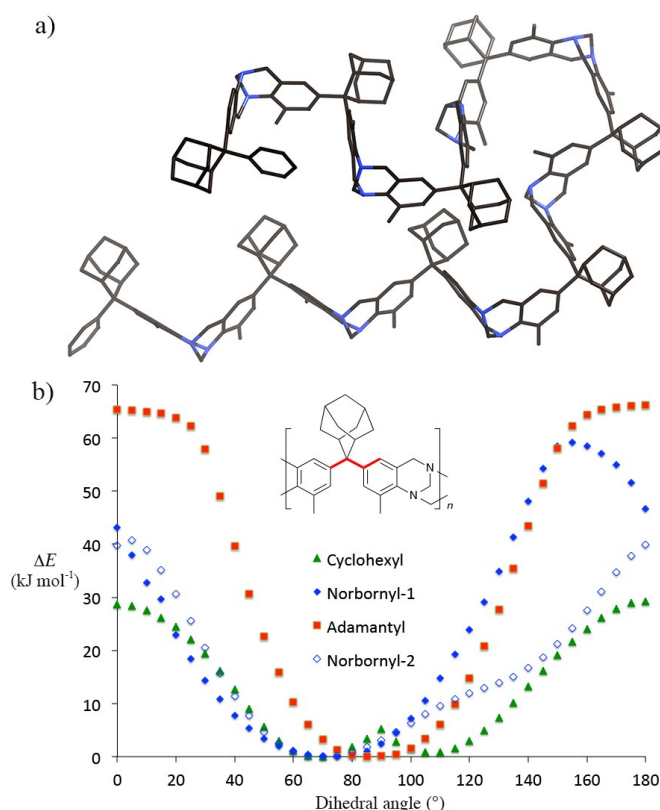


Fig. 3. (a) The contorted chain structure of TB-Ad-Me. (b) The energy profiles for changing the relative conformation of the TB phenyl rings within the repeat unit of the polymer. The relevant dihedral angle is highlighted in red on the structure of TB-Ad-Me.

Table 2. Gas permeabilities P_x , diffusivities D_x , solubility coefficients S_x and ideal selectivities α with respect to N $_2$ at 25 °C for a 125 μ m thick film of TB-Ad-Me. Values for PIM-1 and PIM-EA-TB obtained using similar protocols are also provided for comparison.

Sample	Transport parameters	O $_2$	CO $_2$	CH $_4$	H $_2$	N $_2$
TB-Ad-Me as cast	P_x [Barrer]	40.20	200.5	18.7	161.4	11.24
	α (P_x/P_{N_2})	4.90	24.4	2.02	19.7	-
	D_x [10^{-12} m 2 /s]	27.0	10.3	2.7	695.0	9.1
	S_x [cm 3 (STP) cm $^{-3}$ bar $^{-1}$]	1.12	14.6	4.71	0.17	0.68
TB-Ad-Me After MeOH	P_x [Barrer]	437	1820	162	1800	121
	α (P_x/P_{N_2})	3.62	15.1	1.34	14.9	-
	D_x [10^{-12} m 2 /s]	107.7	41.8	10.1	28205	34.4
	S_x [cm 3 (STP) cm $^{-3}$ bar $^{-1}$]	3.04	32.6	12.0	0.47	2.6
TB-Ad-Me After Ageing (6 months)	P_x [Barrer]	145	635	41	745	33
	α (P_x/P_{N_2})	4.39	19.25	1.25	22.61	-
	D_x [10^{-12} m 2 /s]	45.9	17.9	3.3	1498	12.7
	S_x [cm 3 (STP) cm $^{-3}$ bar $^{-1}$]	2.36	26.65	9.35	0.37	1.95
PIM-1 After MeOH	P_x [Barrer]	2270	13600	1360	5010	823
	α (P_x/P_{N_2})	2.8	16.6	1.7	6.1	-
	D_x [10^{-12} m 2 /s]	512	226	79	>4200	186
	S_x [cm 3 (STP) cm $^{-3}$ bar $^{-1}$]	3.3	45.2	12.9	<0.9	3.3
PIM-EA-TB After MeOH	P_x [Barrer]	2150	7140	699	7760	525
	α (P_x/P_{N_2})	4.1	13.6	1.3	14.8	-
	D_x [10^{-12} m 2 /s]	318	87	36	>7000 ^a	99.5
	S_x [cm 3 (STP) cm $^{-3}$ bar $^{-1}$]	6.0	57.0	14.8	<0.8 ^a	4.7

1 Barrer = 10^{-10} cm 3 (STP) cm cm $^{-2}$ s $^{-1}$ cmHg $^{-1}$

^aFor H $_2$ the very short time lag (<1 s) allows only an estimation of the minimum limit of D and maximum limit of S but are accurate for N $_2$, O $_2$, CO $_2$ and CH $_4$.

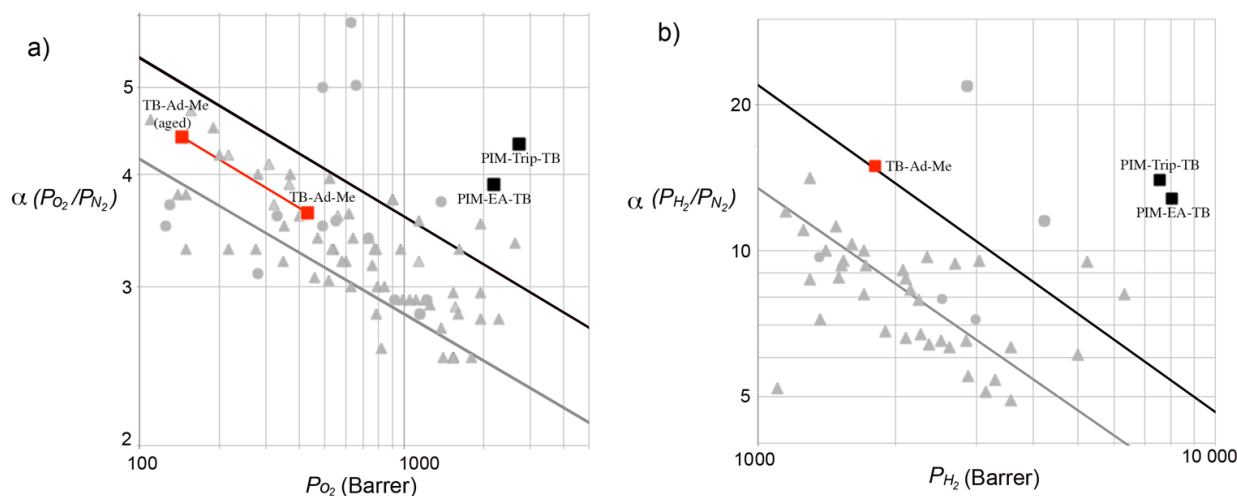


Fig. 4. High permeability portion of Robeson plots for O_2/N_2 and H_2/N_2 with the data for **TB-Ad-Me** highlighted in red. The equivalent data for PIM-EA-TB and PIM-Trip-TB is labelled. The data points that are shaded grey are for other PIMs. The 2008 and 1991 upper bound lines are shown in black and grey, respectively.

pair.²⁵ These upper bounds were updated in 2008.²⁶ The data for **TB-Ad-Me** lie on the 2008 upper bounds for H_2/N_2 and H_2/CH_4 , between the 1991 and 2008 upper bounds for O_2/N_2 and near the 1991 upper bound for CO_2/CH_4 . This performance is typical of that of a PIM (e.g. PIM-1) and is especially encouraging for gas separations involving hydrogen. The exceptional performance of both PIM-Trip-TB and PIM-EA-TB can be attributed to their enhanced rigidity due to a fully fused ladder structure,^{7,8,27} whereas, the single C-C bonds within the chain structure of **TB-Ad-Me** allow some conformational movement (Fig. 3b).

Conclusions

A novel series of cardo-polymers was synthesised using Tröger's base chemistry from bis-aniline monomers derived simply from the condensation of aniline or *o*-toluidine and the cyclic ketones cyclohexanone, norcamphor or 2-adamantanone. The polymerisation of monomers derived from aniline suffered from apparent crosslinking whereas those from *o*-toluidine proceeded smoothly to give high molecular mass polymer. The adamantyl-containing polymer **TB-Ad-Me**, demonstrated significant nitrogen adsorption at 77 K and high gas permeabilities consistent with possessing intrinsic microporosity. This property can be attributed to a more rigid chain structure due to restricted rotation within the bulky adamantyl-based cardo-unit. **TB-Ad-Me** demonstrates promising selectivities for gas separations particularly those involving hydrogen. The ease of synthesis of this polymer – only two steps using readily available precursors – makes it an attractive candidate for further studies as a membrane material.

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